

# Chemical Reclamation for Sodic Strip-Mine Spoils

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## Chemical Reclamation for Sodic Strip-Mine Spoils

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### Summary

Laboratory studies show that hydraulic conductivity of sodic strip-mine spoil is established and maintained at an acceptable level by leaching with high-salt water and that sodic spoil materials can be chemically reclaimed using highly soluble calcium salts. For example, calcium chloride and calcium nitrate are highly soluble calcium salts; gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is not highly soluble.

Sodic soils disperse when treated with low-salt water, and their hydraulic conductivities often are so low that reclamation by leaching is impractical. By using high-salt waters, hydraulic conductivity is established and maintained at an acceptable level, and the leaching solution transports divalent cations to the exchange sites. Laboratory tests indicated that saturated gypsum solution (0.03 normal) did not maintain the hydraulic conductivity of a sodic strip-mine spoil, but with calcium chloride ( $\text{CaCl}_2$ ) solutions greater than about 0.5 normal, the hydraulic conductivity was adequate for reclamation.

Cation-exchange relationships were used to develop an equation for calculating the amount of  $\text{CaCl}_2$  needed to reclaim sodic soils.  $\text{CaCl}_2$  requirement depends on electrolyte concentration of the leaching solution as well as on exchangeable-sodium-percentage, cation-exchange-capacity, and bulk density of the soil. An example shows that the salt required for chemical reclamation of the spoil material used would cost more than \$1,300 per acre per foot of depth reclaimed. On this basis, reclaiming a 5-foot depth of spoil would cost more than \$6,500 per acre. Chemical reclamation of sodic strip-mine spoil material is costly, but the loss of agricultural production is also costly.

Although obviously effective, chemical reclamation is not recommended for large-scale application on strip-mine spoils. Rather, a better alternative is to apply a suitable thickness of nonsodic topsoil and subsoil on strip-mine spoils.

### Introduction

Current surface mining methods tend to invert the soil profile that naturally existed above the deepest mined layer. In the northern Great Plains, the soil material immediately above the deepest layer of lignite coal is generally fine textured, moderately saline, and highly sodic (10).<sup>2</sup> Sodic soils are unstable and have lower hydraulic conductivities than nonsodic soils.

For reclaiming sodic soils by leaching, two conditions must be satisfied: (1) leaching water

must be relatively high in calcium and magnesium ions; and (2) leaching water must percolate through the soil profile so those divalent cations can be transported to the cation-exchange sites for exchange with adsorbed sodium. Waters with low electrolyte concentrations cause sodic soils to disperse and thus cause hydraulic conductivity to diminish. Waters with high electrolyte concentrations, however, have a flocculating effect on the soil particles and cause the clay packets to contract (1, 5). As a result, higher hydraulic conductivities prevail when high-salt waters are used (2, 4, 6, 7, 8).

Gypsum is sometimes applied as an amendment for reclaiming sodic soils. The solubility limit for gypsum in water is only about 0.03 normal. Because of low electrolyte concentration,

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<sup>2</sup> Italic numbers in parentheses refer to Literature Cited, p. 8.

Doering and Reeve (2) found infiltration rate was only 0.03 inches per day for highly sodic Waukena clay loam under laboratory conditions. Similarly low infiltration rates were obtained by Reeve and Doering (9) for the same soil under field conditions. In both experiments, the data clearly indicated that several years would be required to reclaim each foot of soil depth with saturated gypsum solution. On the other hand, data from the field experiment (9) showed that two feet of soil depth could be reclaimed in 3 days with 0.6 normal calcium chloride solution.

Strip-mine spoils are often fine-textured and sodic, but such spoils can be chemically reclaimed by leaching with calcium-rich, high-salt waters.

### Theory

Soil particles have a net negative electrical charge and react chemically with cations—principally calcium (Ca), magnesium (Mg), and sodium (Na)—in the soil solution. The sum total of the exchangeable cations that a particular soil can adsorb is defined as the cation-exchange-capacity (CEC) of that soil (11). A sodic soil is, by definition, a soil that contains sufficient sodium to interfere with the growth of most crop plants—a soil in which the exchangeable-sodium-percentage (*ESP*) is 15 or more (11). Interference with plant growth is usually expressed via the detrimental effect sodium has on soil physical properties rather than as specific toxicity. *ESP* defines the extent to which the adsorption complex of a soil is occupied by sodium.

The *ESP* of a soil is related to the sodium-adsorption-ratio (*SAR*) of its equilibrium soil solution. For most soils, that relationship is expressed approximately (12) by

$$ESP = \frac{100 (-0.0126 + 0.01475 SAR)}{1 + (-0.0126 + 0.01475 SAR)} \quad (1)$$

*SAR* of a soil solution or a leaching water is defined as

$$SAR = \frac{Na}{\sqrt{\frac{Ca + Mg}{2}}} \quad (2)$$

in which the cation concentrations on the right-hand of the equation are all expressed in milliequivalents (meq) per liter.

Previous research (2) indicates that the reaction between the soil adsorption complex and the contacting solution occurs rapidly. To increase the Ca or Mg percentage, or both, on the matrix

Chemical reclamation may be costly, but the loss of agricultural production capacity by not reclaiming the spoils is also costly. The obvious alternative to reclamation is to change mining methods so as to return a suitable depth of native nonsodic surface soil to the surface. By doing so, the agricultural productive potential for the land after mining may be as great as before mining.

The purposes of this publication are to outline the principles involved in the improvement of the chemical and physical characteristics of sodic soils and to approximate the cost of *in situ* reclamation of sodic strip-mine spoils. From such approximations, the value of a foot of nonsodic surface soil can be inferred.

### Theory

exchange sites, that is to reclaim a sodic soil, the *SAR* of the percolating solution must be less than the *SAR* of the equilibrium soil solution at the initially existing *ESP* of the soil. Chemical exchange will occur until the *SAR* of the percolating solution equals the *SAR* of the equilibrium solution. After that, the percolating solution simply passes through the soil without further change in Ca, Mg and Na composition.

Obviously, from equation (2) a solution containing only calcium and magnesium salts has *SAR* = 0. A soil in chemical equilibrium with such a solution would logically have *ESP* = 0. Conversely, a solution containing only sodium salts has *SAR* = ∞, and would be in equilibrium with a soil having *ESP* = 100. Equation (1) is easily described by a semilogarithmic plot using *ESP* on the linear scale (fig. 1). In the range of 3 to 30, *SAR* and *ESP* are numerically about equal. As *ESP* approaches 100, *SAR* increases

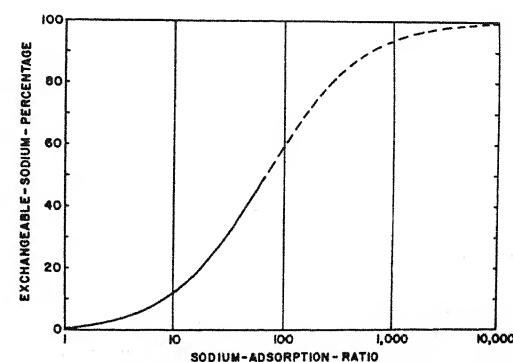


FIGURE 1.—Exchangeable-sodium-percentage as a function of sodium-adsorption-ratio (12).

toward infinity. Because equation (1) was developed using soils that have *ESP*'s ranging from 0 to 50, the curve is shown in figure 1 as a broken line for *ESP*'s greater than 50. For the lack of a proved relationship, however, equation (1) will be assumed to be applicable for all values of *ESP*.

Assuming that the exchange reaction is stoichiometric, the amount of calcium chloride, *W*, needed to reclaim a certain volume of sodic soil is given by the following equation:

$$W = (K) (CEC) (\rho) (F) \quad (3)$$

where

$$F = \frac{ESP}{100(1-C_e)} \quad (4)$$

and where

*K* is a unit conversion constant,

*CEC* is in meq/100 g,

*ρ* is the dry bulk density of the soil in g/cm<sup>3</sup>,

*ESP* is the initial condition expressed as a percentage, and

*C<sub>e</sub>* is the calcium plus magnesium concentration (expressed as a decimal fraction of the total cation concentration) of the equilibrium soil solution corresponding to the initial *ESP* for the soil.

The appropriate value for *K* is 0.755 when *W* is desired in tons of CaCl<sub>2</sub> per acre-foot and 0.555 when *W* is desired in kg per cubic meter. When the soil is initially sodium saturated (*ESP* = 100), *C<sub>e</sub>* will be zero and *F* will be unity.

The significance of *C<sub>e</sub>* is best understood by examining its variation as functions of total salt

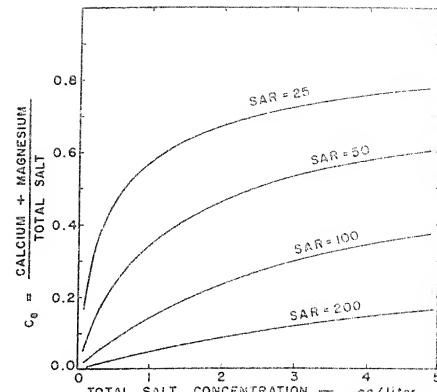


FIGURE 2.—Divalent cation fractions as functions of total salt concentrations and *SAR*.

concentration and various *SAR*'s (fig. 2). *C<sub>e</sub>* increases as total salt concentration increases when *SAR* is held constant and decreases as *SAR* increases when the total salt concentrations is held constant. Because the total salt concentration consists essentially of Ca, Mg, and Na cations,  $(1-C_e)$  represents the Na as a fraction of the total cation concentration. When the leaching solution contains only Ca,  $(1-C_e)$  times the total cation concentration represents the change in Ca concentration because of exchange in the soil.

Because the *SAR* of the percolating solution cannot be reduced to less than the *SAR* of the equilibrium solution, figure 2 defines the calcium plus magnesium concentration of the drainage water. This unusable calcium and magnesium represents an unavoidable duty that must be paid as part of the chemical exchange or reclamation process.

## Materials and Methods

Sodic strip-mine spoil material was used for laboratory determinations of hydraulic conductivity. A saturation extract prepared from a subsample of the spoil material had an electrical conductivity (EC) of 2.9 millimhos/cm, a (Ca + Mg) concentration of 2.3 meq/liter, a Na concentration of 27 meq/liter, and an *SAR* of 25. The *ESP* of the spoil material as calculated by equation (1) was 26. The *CEC* was 24 meq/100 g. Topsoils in this region are generally both nonsaline and nonsodic. Sandoval and others (10) report EC < 1 millimho/cm and *SAR* < 1 for saturation extracts prepared from samples of two normal topsoils. Hydraulic conductivity of these topsoils generally range from 2 to 12 inches per day.

Air-dried and fragmented subsamples of the sodic spoil material were packed in laboratory permeameters that accommodated a soil column 3 inches in diameter and 3.22 inches long. Drainage was provided from the bottom of the soil column through a layer of coarse silica sand. The spoil material was retained above the sand by a fiberglass filter. Four hundred ninety grams (oven-dry basis) of soil were tamped into each permeameter and uniformly packed on a mechanical packer. Packing consisted of 20 drops from a height of 0.9 inch onto a wood block with a 9.2-pound weight on top of the spoil material. The average bulk density for seven samples was  $1.307 \pm 0.013$  g/cm<sup>3</sup>.

Hydraulic conductivity determinations were

made using 0.25-, 0.50-, 1.0-, 1.5-, and 4.4-normal (N)  $\text{CaCl}_2$  solution, saturated gypsum solution (0.03 N), and tap water (0.005 N). Constant hydraulic heads were individually maintained with inverted volumetric flasks operated as Mariotte systems. Hydraulic heads ranged from 5.04 to 5.31 inches. Ambient temperature was  $24.5 \pm$  to  $1.0^\circ \text{C}$ .

Outflow was monitored as a function of time and hydraulic conductivity was determined by method 34b of USDA Handbook No. 60 (12). ( $\text{Ca} + \text{Mg}$ ) concentrations of the leaching waters

and elution samples were determined by EDTA titration. Na concentrations were determined by flame photometry.  $ESP$  was calculated from the  $SAR$  of the saturation extract.  $CEC$  was determined by method 19 of USDA Handbook No. 60 (12).

In a field trial two plots were established. In one plot  $\text{CaCl}_2$  was applied to the soil surface at a rate of 220 tons per acre. No salt was applied to the other plot. Untreated Missouri River water that had a total salt concentration of about 0.007 N was ponded on both plots.

## Results and Discussion

Results of the hydraulic conductivity tests are presented in figure 3. The tests were not replicated and the curve was fitted by eye. Electrolyte concentration had a pronounced effect on hydraulic conductivity, and an electrolyte concentration greater than 0.5 N maintained a suitable hydraulic conductivity for reclamation to proceed at a practical rate.

Electrolyte concentrations for the saturated gypsum solution (0.03 N) and the tap water (0.005 N) were both too low to keep this spoil material from dispersing. The cations in the tap water were about half Na and half ( $\text{Ca} + \text{Mg}$ ). Even though the spoil material samples in the laboratory permeameters were only 3.22 inches long and solution had been continuously ponded on the surface, 127 days had passed and no drainage had occurred from either the gypsum- or tapwater-treated permeameter. In the field trial, more than 16.6 inches of water infiltrated the  $\text{CaCl}_2$ -treated plot in 13 days, but only 1.9 inches infiltrated the nontreated plot.

With the indicated importance of using high-

salt waters for reclamation of sodic spoil materials, the question of the amount of  $\text{CaCl}_2$  becomes important. For this discussion only  $\text{CaCl}_2$  will be considered, but any other calcium salt that is sufficiently soluble in water would be equally usable. Calculations of the amount of  $\text{CaCl}_2$  needed for reclamation depend on three properties of sodic soils, namely  $CEC$ , bulk density, and  $ESP$ , and on the principles of the exchange reaction.

The application of equation (3) is most easily understood by considering first soil with  $ESP = 100$ , that is  $F$  becomes unity, and then considering the magnitude of  $F$  for soils that have  $ESP < 100$ . Knowing  $CEC$  and bulk density, the tons of  $\text{CaCl}_2$  required to reclaim an acre-foot of sodium saturated soil ( $ESP = 100$ ) can be readily calculated. The results of a series of calculations are presented as figure 4 to emphasize the amount of  $\text{CaCl}_2$  that might be involved. For example, for sodium saturated strip-mine spoil material with a bulk density of  $1.3 \text{ g/cm}^3$  and a  $CEC$  of 24 meq/100 g (material of the kind used for the hydraulic conductivity tests), about 24 tons of  $\text{CaCl}_2$  would be required to reclaim one acre-foot.

Evaluation of  $F$ , equation (4), requires that the  $ESP$  of the soil be known.  $ESP$  can be measured in the laboratory, but it is easily evaluated by determining  $SAR$  of the saturation extract and applying equation (1) either arithmetically or graphically via figure 1. Besides, the  $SAR$  of the equilibrium soil solution must be determined and, for practical purposes, can be assumed equal to the  $SAR$  of the saturation extract.

The numerical value of  $F$  is shown in figure 5 as functions of both electrolyte concentration of the leaching solution and  $SAR$  for various equilibrium soil solutions. When  $ESP = 90$ , as shown by

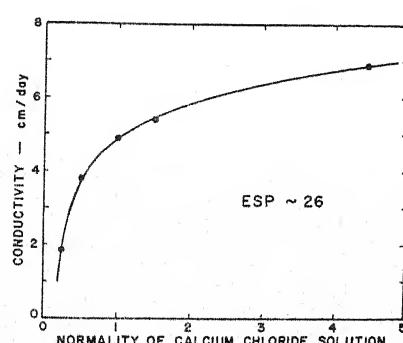


FIGURE 3.—Laboratory hydraulic conductivity of a strip-mine spoil as a function of electrolyte concentration. (Multiply cm/day by 0.4 to get inches per day.)

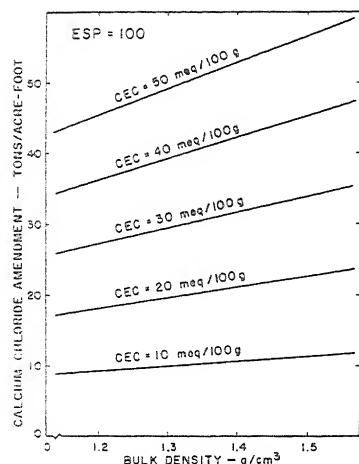


FIGURE 4.—Calcium chloride requirement as a function of bulk density and cation-exchange-capacity when exchangeable-sodium-percentage is 100.

the line for  $SAR = 600$ , electrolyte concentration has almost no effect on the value of  $F$ . As  $ESP$  decreases, however, the curves rotate counter-clockwise and  $F$  increases significantly as the electrolyte concentration increases and  $SAR$  remains constant. The value of  $F$  exceeds 1.0 for high electrolyte concentrations and low  $ESP$  (curve for  $SAR = 25$  with electrolyte concentration greater than 3.5 N) because of the square root in the equation for  $SAR$ .  $F > 1.0$  simply means that the percentage of Ca that can be extracted from a particular solution by a soil is less than the  $ESP$  of the soil.

Leaching processes that have low values of  $F$  will require less  $\text{CaCl}_2$  than processes that have higher values of  $F$ . Hence, the least investment for chemical amendment will be associated with the lowest electrolyte concentrations that can be used, but hydraulic conductivity also is lowest with the lowest electrolyte concentration. For example, if  $SAR$  of the equilibrium soil solution is known and 0.75 N is accepted as the lowest electrolyte concentration at which hydraulic conductivity will be acceptable, the appropriate value of  $F$  can be obtained from figure 5.

For the strip-mine spoil material with  $SAR = 25$  for the equilibrium soil solution, the value of  $F$  is 0.56 when the leaching solution is 0.75 N  $\text{CaCl}_2$ . From equation (3),  $W$  will equal 13.2 tons of  $\text{CaCl}_2$  per acre-foot of soil when  $CEC = 24$  meq/100 g and  $\rho = 1.3 \text{ g/cm}^3$ . If the leaching solution were 4.5 N,  $F$  would be 1.13 and the  $\text{CaCl}_2$  requirement would be 26.6 tons per acre-foot—twice the  $\text{CaCl}_2$  requirement with 0.75 N solution.

An application of 13.2 tons of  $\text{CaCl}_2$  per acre as 0.75 N solution would require 2.8 inches of water. Application by surface irrigation methods would necessitate precise land leveling. Application by sprinkler would be easier but the solution would be corrosive and increase system maintenance requirements. The easiest application method would be to apply the  $\text{CaCl}_2$  to a nearly level soil surface, mix it with the upper inch or so of soil, and apply water naturally or artificially. For such a reclamation scheme, the electrolyte concentration at the wetting front would be unknown, but it would undoubtedly be high; and the  $\text{CaCl}_2$  requirement would be considerably higher than when the electrolyte concentration were controlled at a lower level as was shown in the previous paragraph.

Because of their inherent physical properties, sodic strip-mine spoils represent both an inhospitable environment for plant roots and a barrier to the downward percolation of water. As a consequence, the depth of chemical reclamation, or the depth of topsoil returned, becomes the effective root zone. The depth chosen depends on the agricultural productive potential that is to be provided for the future. Greater depth means greater soil-water storage capacity that often means more available water to carry the crop through extended dry periods. The rooting habits of agricultural plants differ, but many crops can withdraw water from depths of 5 feet or more. Research is currently underway at the Northern Great Plains Research Center to determine what the reclamation, or restoration, depth should be for optimum agricultural productive capacity.

Precipitation percolating through natural sur-

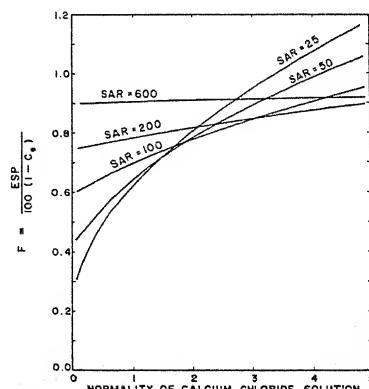


FIGURE 5.—Effect of electrolyte concentration on the quotient of  $ESP$  and the decimal fraction of the divalent cations that are extractable from a leaching solution.

face soils or reclaimed spoils would have a low electrolyte concentration. Sodic spoils would have very low permeability to such water and might cause a perched water table to develop in the reclaimed or restored soil when infiltration exceeded crop use. A perched water table is beneficial when that water is available to plants and detrimental when it causes the root zone to become water-logged and poorly aerated either directly by downward percolation to the sodic material or indirectly by lateral flow above the sodic material within the subsurface drainage system. Shallow depths of reclamation or restoration provide a smaller reservoir for water storage and, as a result, are more subject to water-logging than deeper depths of reclamation or restoration.

One way to arrive at a minimum depth of reclamation is to examine the unsaturated flow properties of typical soils and determine the depth the water table (herein analogous to the top of the sodic material) should be maintained to cause evaporation from a fallow surface to be

less than about 0.04 inch per day. The 0.04 inch per day chosen for the evaporation rate is about 15 percent of the potential evaporation expected on a hot summer day in the northern Great Plains. Using theory developed by Gardner (3) and data published by Willis (13) the water table would need to be at least 4.3 feet below the surface in a loam soil to keep the upward flow rate, that is the evaporation rate, less than 0.04 inch per day. If the water table were 2 feet below the surface in that loam soil, the potential rate of evaporation from the surface would be about 0.2 inch per day, about two-thirds the expected evaporation from a free water surface on a hot summer day. Such calculations indicate that the practical minimum depth of reclamation or restoration should be about 5 feet. Obviously, when chemical reclamation is used, the depth of treatment should be sufficient to prevent resalinization by upward movement of salts associated with water movement because of evaporation during extended periods without rainfall.

### Conclusions

Reclamation of sodic soils by leaching requires (1) that the leaching solution be high in divalent cations (Ca or Mg or both), and (2) that the leaching solution must percolate through the soil profile to transport those cations to the exchange sites. Sodic soils tend to disperse when they are treated with waters having low electrolyte concentrations. As a consequence, hydraulic conductivities are usually so low that reclamation by leaching with low-salt waters becomes impractical if not impossible. High-salt waters, on the other hand, act as flocculants and cause even highly sodic soils to remain permeable.

Sodic strip-mine spoil material can be readily reclaimed with solutions of  $\text{CaCl}_2$  or any other calcium salt that is sufficiently soluble in water, having electrolyte concentrations greater than about 0.5 N. The amount of salt needed for reclamation depends on the salt concentration in the leaching solution as well as on the CEC, bulk density, and *ESP* of the soil. For soils having  $ESP < 75$ , the amount of  $\text{CaCl}_2$  required for reclamation increases significantly as electrolyte concentration increases. The reclamation process, then becomes a balance between keeping the electrolyte concentration low to minimize the  $\text{CaCl}_2$  requirement and keeping the electrolyte concentration high to maintain permeability.

Reclamation costs represent one measure of the value of agricultural soil. For a sodic strip-mine spoil material with  $ESP = 26$ ,  $CEC = 24$  meq/100 g, and bulk density = 1.3 g/cm<sup>3</sup> that is leached with 0.75 N  $\text{CaCl}_2$ , 13.2 tons of  $\text{CaCl}_2$  will be required to reclaim each acre-foot. Increasing the electrolyte concentration to 4.5 N reduces reclamation time but doubles the  $\text{CaCl}_2$  requirement.

At an assumed price of \$100 per ton for  $\text{CaCl}_2$ , the salt required for reclaiming would cost over \$1,300 per acre per foot of soil depth using 0.75 N  $\text{CaCl}_2$  solution and over \$2,600 per acre per foot of soil depth using 4.5 N  $\text{CaCl}_2$  solution. Chemical reclamation of sodic strip-mine spoils is obviously costly, but reclamation cost is a distinct indicator of the value of natural nonsodic surface soils. The foregoing discussion deals only with the cost of salt for chemical reclamation. Land leveling, water, water handling, and related costs would be added to get a true total cost. If chemical reclamation alone costs over \$1,300 per acre foot, then an acre-foot of nonsodic surface soil is worth at least \$1,300 and 5 feet of nonsodic surface soil on an acre of land is worth at least \$6,500. Other inherent properties of the natural nonsodic surface soil, such as organic matter and plant nutrients, increase its value even more.

For spoils with *CEC* greater than the 24 meq/100 g used in the above example, both  $\text{CaCl}_2$  requirement and reclamation cost will be correspondingly increased. Although obviously effective and a necessary first step in reclamation of

existing sodic spoils, chemical reclamation is not recommended for large-scale application to strip-mine spoils. Rather, utilization of a suitable thickness of naturally occurring nonsodic topsoil and subsoil, replaced on spoil material, is obviously a better alternative.

### Acknowledgment

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